A fluctuation theorem for phase turbulence of chemical oscillatory waves

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Through numerical simulations of the Kuramoto equation, which displays high-dimensional dissipative chaos, we find a quantity representing the cost for maintenance of a spatially non-uniform structure that appears in the phase turbulence of chemical oscillatory waves. We call this quantity the generalized entropy production and demonstrate that its distribution function possesses a symmetry expressed by a fluctuation theorem. We also report a numerical result which suggests a relation between this generalized entropy production rate and the Kolmogorov-Sinai entropy.

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When a system exists in a non-equilibrium steady state, the entropy produced in the system continuously flows into the environment. The amount of the entropy produced during a finite time interval is called the 'entropy production'. As stipulated by the second law of thermodynamics, the entropy production must be positive.

Entropy production can be interpreted as the cost for the maintenance of non-equilibrium steady states. This leads us to expect that we can find a quantity which can be regarded as a *generalized entropy production* characterizing non-thermodynamic as well as thermodynamic systems. With the hope of demonstrating this point, we study the phase turbulence of chemical oscillatory waves [1].

When a pacemaker is situated in a small region in a spatially uniform phase turbulent state, a spatially non-uniform state appears, as is easily understood. In this paper, through numerical experiments, we find an expression for a generalized entropy production characterizing such a spatially non-uniform state. We further attempt to relate this generalized entropy production with the Kolmogorov-Sinai (KS) entropy, which measures the rate of information loss in chaotic dynamical systems.

We first introduce a mathematical model describing phase turbulence. For simplicity, we consider reaction diffusion systems in a one-dimensional circuit. Such systems are considered as describing the behavior of the concentrations of chemical species. For a system of this type, when certain conditions are satisfied (see [1] for details), their concentrations oscillate at each position x, and the phase ϕ of the oscillation varies slowly in time t. In the weakly unstable case, the time evolution of the phase $\phi(x, t)$ is described by the Kuramoto equation [1, 2],

$$\frac{\partial \phi}{\partial t} + \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^4 \phi}{\partial x^4} + \frac{1}{2}\left(\frac{\partial \phi}{\partial x}\right)^2 = \epsilon \omega(x), \qquad (1)$$

where we have carried out appropriate scalings for x, t and ϕ so as to obtain the simplest form of the equation.

The Kuramoto equation (1) is defined over the region $0 \leq x \leq L$, with periodic boundary conditions. The right-hand side of (1) represents the effect of external oscillation introduced by the pacemaker: ϵ corresponds to the pacemaker strength, and the form of $\omega(x)$ reflects its position. We assume that $\omega(x) = 1$ in the region $0 \leq x \leq H$ and $\omega(x) = 0$ otherwise. In the analysis below, we study the case $(L, H) = (128, 10)$.

We obtain an expression for the generalized entropy production by undertaking a numerical analysis of (1). In our numerical simulations, we discretized space with a unit size $\delta x = 1.0$ and employed an explicit Euler method with time step $\delta t = 0.01$. The nonlinear term was discretized as $((p_{i+1} - p_{i-1})/2\delta x)^2/2$, where $p_i = \phi(i\delta x, t)$. We believe that this numerical scheme is sufficient to allow for investigation of the behavior of interest.

When there is no pacemaker ($\epsilon = 0$), (1) possesses spatio-temporal chaotic solutions for a rather wide class of initial conditions [1, 3]. (Precisely speaking, there is a very small basin for stable spatially periodic solutions [4, 5, 6]. However, we do not consider such solutions, because this basin is too small to be observed when initial conditions are assigned randomly [6].) The statistical properties of this spatio-temporal chaos have been extensively studied both numerically [3, 4, 7] and theoretically [8, 9].

When $\epsilon \neq 0$, the system possesses spatially non-uniform statistical properties. As an example, in Fig. 1, we plot the long-time average of the phase profiles, each of which is shifted so as to satisfy $\phi(0, t) = 0$.

Now, let us consider the generalized entropy production which represents the cost for maintaining the spatially non-uniform state. It is important to note here that the generalized entropy production will not be expressed in terms of heat, in contrast to the usual entropy production of non-equilibrium steady states, because the phase turbulent state cannot be described by quantities characterizing thermodynamic equilibrium states. For this reason, we have no intention to base our analysis of the generalized entropy production on thermodynamic considerations. Instead, we consider a more abstract condition that we expect the generalized entropy production to satisfy.
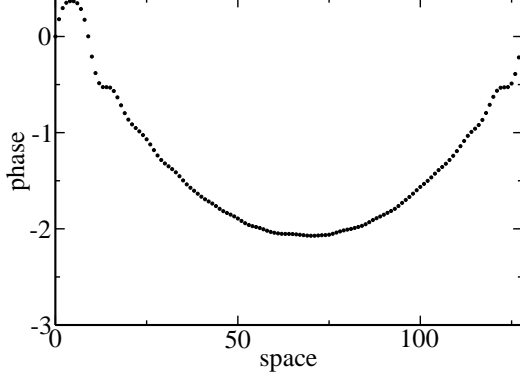
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FIG. 1: Long time average of the phase profiles, each of which is shifted so as to satisfy $\phi(0,t) = 0$. Here, $\epsilon = 0.1$. The averaging time was 4×10^7 time units for the statistical steady state.
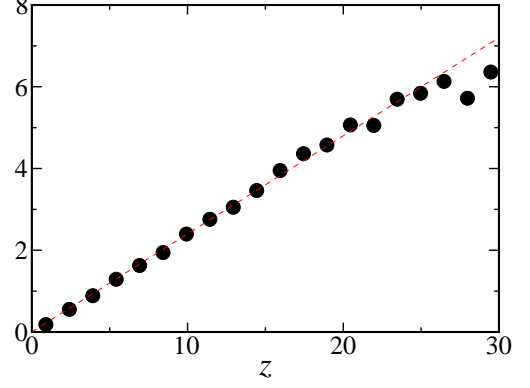

FIG. 2: $\log \Pi(z;\tau,1) - \log \Pi(-z;\tau,1)$. The dotted line corresponds to $\log \Pi(z;\tau,1) - \log \Pi(-z;\tau,1) = 0.24z$. Here, $\epsilon = 0.1$ and $\tau = 200$. The distribution was made by using 2×10^5 trajectory segments for the statistical steady state.

As a recent development in the study of non-equilibrium steady states [10, 11, 12, 13], an interesting relationship regarding the entropy production has been established. Defining $\Pi(z;\tau)$ to be the probability density that the entropy production Σ_τ during a finite time interval τ takes the value z in a given non-equilibrium steady state, it has been shown that this probability density possesses the symmetry

$$\log \Pi(z;\tau) - \log \Pi(-z;\tau) = z + o(\tau) \qquad (2)$$

in the limit $\tau \to \infty$. This symmetry is referred to as a 'fluctuation theorem'. From (2), it is easily derived that the most probable value of the entropy production ratio Σ_τ/τ in the large τ limit is positive. Considering the above result for entropy production in non-equilibrium steady states, we conjecture that a similar result can be obtained for a wider class of nonequilibrium states by appropriately defining a generalized entropy production and seeking a generalized fluctuation theorem it satisfies.

The problem we face is to find a generalized entropy production characterizing spatially non-uniform phase turbulent states, whose distribution function satisfies (2). By recalling that the entropy production in a non-equilibrium steady state can be expressed in the form [force][flux]/[temperature], and by interpreting $\epsilon \partial_x \omega$ and $\partial_x \phi$ as corresponding to a force and a flux, we regard the following quantity as a candidate of the generalized entropy production:

$$\Sigma_\tau^{\mathrm{K}} = \epsilon \beta \int_0^\tau dt \int_0^L dx (-\omega(x)) \frac{\partial^2 \phi}{\partial x^2}, \qquad (3)$$

where we note that the integrand in (3) is rewritten as $\partial_x \omega \partial_x \phi$. β corresponds to the effective inverse temperature of the phase turbulence whose value is determined later so that the distribution function of Σ_τ^{K} satisfies (2).
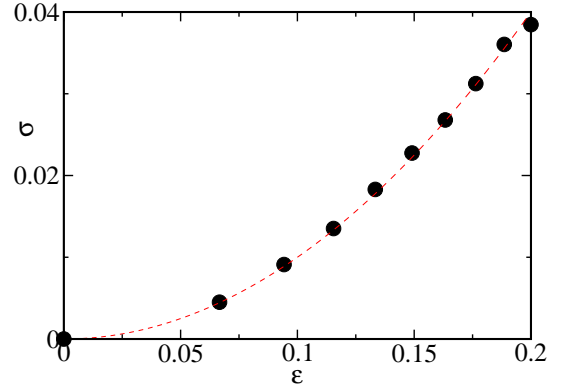
FIG. 3: Entropy production rate σ as a function of ϵ. The dotted line corresponds to $\sigma = \epsilon^2$. The averaging time was 4×10^5 time units for the statistical steady states.

Through numerical experiments, we obtained the distribution function $\Pi(z;\tau,\beta)$ of Σ_τ^{K} for a statistically steady state. Since the value of β is not determined yet, we first considered an arbitrary value and calculated $\Pi(z;\tau,1)$. As seen from Fig. 2, it seems that the equality

$$\log \Pi(z;\tau,1) - \log \Pi(-z;\tau,1) = 0.24z \qquad (4)$$

holds approximately. Then, since the trivial identity

$$\Pi(z;\tau,\beta) = \Pi(z/\beta;\tau,1)/\beta \qquad (5)$$

holds, $\Pi(z;\tau,\beta)$ with $\beta = 0.24$ satisfies the fluctuation theorem (2).

If we wish to characterize spatially non-uniform phase turbulence by a single quantity, the generalized entropy

production ratio,

$$\sigma = \lim_{\tau \to \infty} \frac{\Sigma_\tau^{\mathrm{K}}}{\tau}, \qquad (6)$$

may be most important. In Fig. 3, we plot σ as a function of the pacemaker strength ϵ. As is true generally for non-equilibrium steady states, we see that σ is proportional to ϵ^2 in the region of small ϵ.

We can formulate an argument to support our numerical result by considering the Yakhot conjecture [9, 16, 17, 18] that the long time and large distance behavior of statistical properties of chaotic solutions to (1) are equivalent to that of solutions to the stochastic evolution equation (which is essentially the same as the Burgurs equation with noise)

$$\frac{\partial \tilde\phi}{\partial t} - \nu \frac{\partial^2 \tilde\phi}{\partial x^2} + \frac{\lambda}{2}\left(\frac{\partial \tilde\phi}{\partial x}\right)^2 = \epsilon\omega(x) + \xi, \qquad (7)$$

where ξ is a Gaussian white noise satisfying

$$\langle \xi(x,t)\xi(x',t')\rangle = 2D\delta(t-t')\delta(x-x'). \qquad (8)$$

Here, ν and D are positive constants. It is quite easy to demonstrate a fluctuation theorem for this stochastic system (See Refs. [12, 13]). The result is the following: When we define the entropy production as

$$\Sigma_\tau^{\mathrm{B}} = \epsilon \frac{\nu}{D} \int_0^\tau dt \int_0^L dx (-\omega(x))\frac{\partial^2 \tilde\phi}{\partial x^2}, \qquad (9)$$

the distribution function of Σ_τ^{B} for a statistical steady state satisfies the fluctuation theorem (2). Therefore, if the Yakhot conjecture is valid and if this conjecture ensures the equality of the space-time inetegration in (3) with that in (9), the expression of (3) should hold with $\beta = \nu/D$.

We would like to consider the generalized entropy production from the dynamical system viewpoint. Until now, we have not succeeded in deriving the fluctuation theorem in a manner based on dynamical system considerations. However, we have obtained a numerical result concerning the relation between the generalized entropy production rate and the KS entropy, which can be calculated using the Lyapunov analysis. We now discuss this result.

Performing numerical integrations of the linearized equation corresponding to (1) for chaotic solutions and employing the Gram-Schmidt decomposition technique [14], we calculated the long time average of the expansion ratio, $\Lambda(m)$, for m-dimensional volume elements along chaotic trajectories [4]. In Fig. 4, the graph of $\Lambda(m)$ is plotted for the system without the pacemaker. The KS entropy is defined as the maximal value of $\Lambda(m)$. Let $h_{\mathrm{ks}}(\epsilon)$ be the KS entropy for the system with pacemaker strength ϵ. Since we naively expect that $\sigma(\epsilon)$ is related to the quantity

$$\Delta h_{\mathrm{ks}}(\epsilon) = h_{\mathrm{ks}}(\epsilon) - h_{\mathrm{ks}}(0), \qquad (10)$$
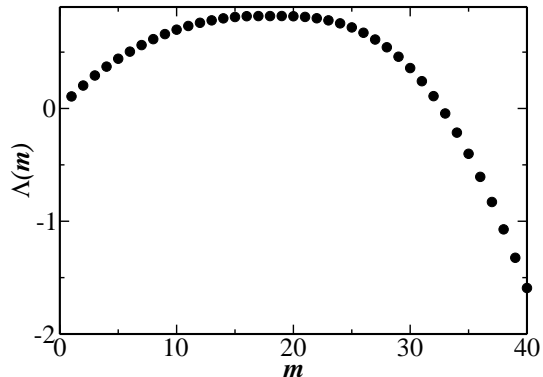

FIG. 4: Long time average of the expansion ratio of m-dimensional volume elements. The averaging time was 10^4 time units for the statistical steady state.
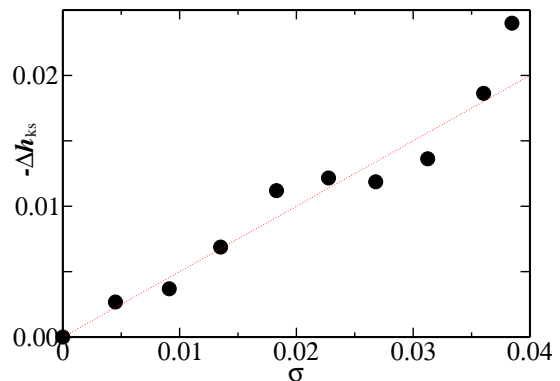

FIG. 5: $(\sigma, -\Delta h_{\mathrm{ks}})$ for different values of ϵ ($0 \le \epsilon \le 0.2$). The dotted line corresponds to $-\Delta h_{\mathrm{ks}} = \sigma/2$. The averaging time was 4×10^5 time units for the statistical steady states.

we plot points $(\sigma, -\Delta h_{\mathrm{ks}})$ for different values of ϵ. As displayed in Fig. 5, the results indicate the relation

$$-\Delta h_{\mathrm{ks}} = \frac{1}{2}\sigma \qquad (11)$$

for small ϵ. Note that we observed a greater deviation from (11) when ϵ is increased.

We do not understand why the numerical factor $1/2$ appears in (11). However, the fact we have obtained such a simple relationship for the system we consider presently may suggest the existence of a universal relation between the generalized entropy production and some dynamical system quantity. (In the study of a time-dependent Hamiltonian system, the same factor appears in the relation between the Boltzmann entropy difference and the

excess information loss found through Lyapunov analysis [15].) Further investigation is necessary to clarify this point.

We now make some remarks.

A fluctuation theorem was first demonstrated numerically [10] and proved mathematically [11] in the study of a deterministic Gaussian thermostatted model. In this model, the entropy production is given by the phase space contraction, and the fluctuation theorem is derived by exploiting the time-reversibility of the deterministic evolution equation. Indeed in many cases, including that of the stochastic model (7) with (8), the entropy production for a given trajectory has been related to the ratio of the measure of this trajectory to that of its time reversal trajectory. However, such an argument cannot be applied to (1), because it does not possess time-reversal symmetry.

On a more abstract level, as discussed by Maes [13], fluctuation theorems can be associated with a transformation P, that acts on trajectories and satisfies $P^2 = 1$. In certain situations (e.g. for steady states), this transformation is equivalent to time reversal, but in general this is not the case. The problem is thus to determine the form that P takes in the present case and to determine how to derive our fluctuation theorem from it.

Finally, we briefly discuss the size dependence for the system we have studied. It is known that the statistical properties of phase turbulence without a pacemaker depend on L in an anomalous way [8, 9, 16, 17, 18]. The system size in our numerical experiments is much smaller than the size representing cross-over to the region in which the anomalous behavior is observed. It is an interesting problem to extend our study to this anomalous scaling region.

In summary, we have demonstrated that the generalized entropy production (3), which has been obtained phenomenologically in the consideration of spatially non-uniform phase turbulent states, satisfies the fluctuation theorem (2). Unfortunately, there is no obvious way to derive this fluctuation theorem from the deterministic evolution equation in the present case, because we cannot employ an argument relying on time-reversibility. Nevertheless, using the Yakhot conjecture, we have formulated a reasonable explanation of the result. We have also obtained the numerical result (11), which suggests an interesting relation between the generalized entropy production ratio and the KS entropy. We believe that a deeper understanding of the problem considered here will allow for the study of dissipative high-dimensional systems, such as fluid turbulence and granular flow, from a new point of view.

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